SUPPLEMENTARY INFORMATION

Linkage between solid phase apportionment and bioaccessible arsenic, chromium and lead in soil from Glasgow, Scotland, UK.

|Joanna Wragg[a]*, Andrew Broadway[c],, Mark R. Cave[a], Fiona M. Fordyce[b], Barbara Palumbo-Roe[a] Darren J. Beriro[a], John G. Farmer[c], Margaret C. Graham[c], Bryne T. Ngwenya[c], Richard J.F. Bewley[d]

[a]British Geological Survey, Environmental Science Centre, Keyworth, Nottingham, NG12 5GG, UK

[b] British Geological Survey, The Lyell Centre, Research Avenue South, Edinburgh, EH14 4AP, UK

[c]School of GeoSciences, University of Edinburgh, Edinburgh, EH9 3JN, UK

[d] URS Corporation Ltd, Manchester, M1 6HS, UK

*Corresponding author. Tel+44 (0)115 936 3069; fax+44 (0)115 936 3460. E-mail address: jwrag@bgs.ac.uk

Table S1 Detailed description geochemical clusters and groupings

Cluster name	Cluster number	Median composition (%)	Aqua Regia concentration range	Sample groups	Comments
Residual pore salts	C1	Na (37%), S (37%), Ca (4%), Fe (3%), Si (2%), K (1%)	DI	1 & 2	Extracted by de- ionised water only, this highly mobile cluster is likely to be derived from residual pore salts
Organic	C2	S (70%), Si (7%), Fe (2%)	DI – 5.0M	2	The shape of the extraction profile is indicative of the presence of humic acid as the cluster is initially dissolved in de-ionised water becoming insoluble on the addition of acid. As the acid concentration increases and H_2O_2 added, humic acid is oxidised and breaks down, to be observed in the latter parts of the extraction profile. On the breakdown of this component the inorganic content of the cluster is released into solution, in this case Fe, As and Ni
Exchangeable	C3	K (30%), Mg (11%) Ca (8%), S (5%), Na (4%), Mn (2%)	DI – 0.01M	1, 2 & 3	The cluster only makes a small contribution to the total amount of solids extracted by the CISED method. Its composition and ease of extraction of this component is suggestive that the individual components associated with this cluster are exchangeable (Rowell 1994).

Cluster name	Cluster number	Median composition (%)	Aqua Regia concentration range	Sample groups	Comments
Mg-dominated	C4	Mg (62%), Ca (20%), Fe (6%), S (4%), K (2%)	DI – 0.05M	3	The primary hosts of Cr (1398 mg kg^{-1}) in the 27 soils. This is probably as a result of the presence of Mg bearing minerals (e.g. brucite, $MgOH_2$) and chromite (Fe, Mg)Cr_2O_4 which are constituents of COPR
	C14	Mg (53%), Al (21%), Fe (9%), Mn (7%), Ca (2%), P (1%)	0.1 – 5.0M	2	
	C15	Mg (45%), Al (17%), Fe (15%), Ca (12%)	0.01 – 1.0M	3	

Cluster name	Cluster number	Median composition (%)	Aqua Regia concentration range	Sample groups	Comments
Ca-dominated	C5	Ca 90%), Mg (6%), Si (1%)	0.01 – 1.0M	1 & 2	The composition and ease of extraction identifies these as three separate clusters. Although only a small proportion of the samples were collected from sites containing the highly alkaline (Ca and Mg dominated) COPR waste, it has had an impact on the mineralogy of these soils. The increased acid strength along with the composition of C7 has given rise to the name 'High Ca-Mg carbonate'. Previous application of the CISED extraction to other soils (e.g. (Cave et al. 2015)) has revealed that some physico-chemical components can be bound or encapsulated by another component. For example, a carbonate component encased by Fe-oxide would not be extracted until the application of higher acid strengths required for the dissolution of the Fe-oxide. That being the case, C7 is likely to be associated with a more acid-stable cluster, in this case possibly C15 or C16. The C7 cluster is only found in the Group 3 soil (Figure 8), the single soil in this group from Rutherglen with COPR (with high concentrations of Ca and Mg) contamination.
	C6	Ca (69%), Al (7%)	0.01 – 1.0M		The PHE were distributed within the combined carbonate clusters (C5+ C6 + C7) equating to 5.86, 4.98 and 1.53 % of the total extractable element content. Potential host geochemical phases for As in this study are calcium carbonate minerals, but the amount of As accounted for compared to Fe-oxides is small. It is known, however, that As commonly substitutes for P in Ca-phosphate mineral phases e.g. apatite (Drahota and Filippi 2009; Smedley and Kinniburgh 2002). Several carbonate related clusters contain Cr (Table 4), a probable result of the use of lime in chromite ore processing (Hillier et al. 2003). Lead in the Ca-dominated phases may be associated with the presence of phosphates (Pb-PO4 minerals) and/or carbonates e.g. cerussite ($PbCO_3$). A previous study of sequential extraction of heavy metals from Glasgow soils (Gibson and Farmer, 1986) identified that although a large proportion of Pb was associated with residual geochemical phases, 13% of the Pb was associated with the exchangeable and carbonate phases combined.
	C7	Ca (89%), Mg (10%)	0.01 – 1.0M	3	

Cluster name	Cluster number	Median composition (%)	Aqua Regia concentration range	Sample groups	Comments
Al-Si-dominated	C8	Al (36%), Si (34%), Ca (10%), Fe (10%), Mg, Mn, P (1 – 5%)	DI – 1.0M	2	Two clusters were identified as alumino-silicate materials and make up the third largest cluster type e.g. the cluster with the widest range (Figure 7). Extraction of both C8 and C9 was less well defined compared to the other clusters. When combined, the Al-Si dominated clusters (C8 + C9) are the primary hosts of Pb and a significant host of As (Table 4). Both As and Pb can be sorbed onto alumina-silicate minerals in soils (Alloway 2013; Goldberg 2002) with Pb showing the strong affinity to clays (Bradl 2004).
	C9	Al (53%), Fe (11%), P (2%), Ca (2%), Si (3%), Mg and Mn (<1%)	0.05 – 5.0M	1 & 2	

Cluster name	Cluster number	Median composition (%)	Aqua Regia concentration range	Sample groups	Comments
Mn oxide	C10	Mn (40%), Al (21%), Ca (20%), P (4%), Si (4%)	0.1 – 1.0M	1 & 2	Figure 6 shows that C10 has a high concentration of Mn and is first observed on the addition of H_2O_2 (step 7) to the system, a reagent known to readily dissolve Mn oxides, providing supporting evidence suggesting that C10 is derived from Mn oxides. The Mn oxide cluster was host to a small proportion 0.01% and 1.88% of the total extractable Cr and Pb respectively, but not As. This association is a likely result of the metal absorbing capability of Mn oxides, in particular Pb (Alloway 2013; McKenzie 1980).
P-dominated	C11	P (65%), S (11%), Fe (5%), Al and Si (2 – 3%)	0.01 – 5.0M	2	Arsenic and Pb can both substitute into phosphate minerals especially apatite, with Pb forming phosphate minerals like pyromorphite (Alloway 2013).

Cluster name	Cluster number	Median composition (%)	Aqua Regia concentration range	Sample groups	Comments
Fe-dominated	C12	Fe (43%), Al (20%), Ca (14%), S (6%), P (4%), Si (2%), Mg (2%), Mn (1%)	0.01 – 5.0M	1, 2 & 3	All of the clusters are dominated by the presence of Fe with smaller contributions from other elements e.g. Al (C16 and C12). C13 is extracted over a wider window than C16 and C12, which have narrow windows of extraction and observed later in the CISED scheme. The differences in the extractograms are likely to be a result of both physical and chemical differences in the cluster components, e.g. the other associated elements and the amount of each. The dominance of Fe with the mid-high acid strength required for their removal indicates that C16, C13 and C12 are likely to be Fe-oxides. Two of the clusters identified as Fe-oxides (C13 and C16) act as hosts for As, Cr and Pb in the soils (Table 4); Cr was the only PHE distributed within cluster C12. This association of As, Cr and Pb with Fe-oxides is shown widely in the literature e.g. Fe-oxides form a particularly strong relationship with As (Alloway 2013; Goldberg 2002) and Fe-oxides exhibit a strong affinity with Cr and exert a predominant role on Pb adsorption in soils (Bradl 2004).
	C13	Fe (34%), Mn (2%) Al (1%), P (1%)			
	C16	Fe (77%), Al (10%), Mg, (3%) P (3%), S (2%), Si (2%)			

References

ALLOWAY, B J. 2013. *Heavy Metals in Soils*. (Netherlands: Springer) ISBN 978-94-007-4469-1
BRADL, H B. 2004. Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, Vol. 277, 1-18.
CAVE, M, WRAGG, J, GOWING, C, AND GARDNER, A. 2015. Measuring the solid-phase fractionation of lead in urban and rural soils using a combination of geochemical survey data and chemical extractions. *Environmental Geochemistry and Health*, Vol. 37, 779-790. 10.1007/s10653-015-9697-9
DRAHOTA, P, AND FILIPPI, M. 2009. Secondary arsenic minerals in the environment: A review. *Environment International*, Vol. 35, 1243-1255.
GIBSON, M J, AND FARMER, J G. 1986. Multi-step sequential chemical extraction of heavy metals from urban soils. *Environmental Pollution Series B, Chemical and Physical*, Vol. 11, 117-135.
GOLDBERG, S. 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. *Soil Science Society of America Journal*, Vol. 66, 413-421.
HILLIER, S, ROE, M J, GEELHOED, J S, FRASER, A R, FARMER, J G, AND PATERSON, E. 2003. Role of quantitative mineralogical analysis in the investigation of sites contaminated by chromite ore processing residue. *Science of the Total Environment*, Vol. 308, 195-210.
MCKENZIE, R. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Soil Research*, Vol. 18, 61-73.
ROWELL, D L. 1994. *Soil Science, Methods and Applications*. (Longman Scientific & Technical.)
SMEDLEY, P L, AND KINNIBURGH, D G. 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, Vol. 17, 517-568.